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Fluorescence spectroscopy as a non destructive method to predict rheological characteristics of Tilsit cheese

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The objective of this study was to investigate the potential of fluorescence spectroscopy to predict rheological characteristics of semi-hard cheeses as yield stress (τ_L), flow stress (τ_F), storage modulus (G') and loss modulus (G'') measured at linear-viscoelastic, yield stress and flow stress oscillation regions. Melting temperatures and chemical composition of the semi-hard cheeses were also predicted using fluorescence spectra. Principal component analysis (PCA) and partial least squares regression (PLSR) were applied to the fluorescence spectra to extract information on the rheological properties, chemical composition, and melting temperatures. τ_L and τ_F were predicted with $R^2 = 0.90$ from the vitamin A emission and excitation spectra, respectively. Melting temperatures, moisture, protein and fat contents were predicted with $R^2 = 0.98$ from the vitamin A emission spectra. This study demonstrates that fluorescence spectroscopy has potential for the accurate, non-destructive and rapid prediction of cheese rheology at linear-viscoelastic, yield stress and flow stress oscillation regions simultaneously.

1. Introduction

Cheese is used as a final product in the human diet, as well as an important ingredient in various foods to form desirable texture, taste, flavor and nutritional value. The use of cheese as an ingredient is affected by complex physical, thermal and mechanical processes (John, 2008; Subramanian et al., 2006). The rheological properties of cheese undergo significant changes in relation to temperature, duration and intensity of mechanical stress, method of transportation as well as changing shear rate (O'Callaghan and Guinee, 2004). Since the cheese is exposed to these different factors, the study of rheological behavior of cheeses in a wide range of the shear stress, i.e. in linear visco-elastic (LVE), yield stress, and flow stress regions becomes a task of critical importance.

In the LVE range small sinusoidal stresses or strains are applied to a cheese sample at levels that do not cause significant irreversible changes to the cheese internal structure. The LVE range is characterized by viscous (G'') and elastic (G') moduli the values of which remain unchanged throughout the LVE region indicating that the microstructure of the cheese is undisturbed. Therefore the LVE region is suitable for probing cheese structure and structure development during different processes. The Yield Stress region shows a significant change in the structure of the material. It also indicates the start of plastic deformation when a breakdown occurs, consequently, modulus decreases. The Flow Stress region can be used to determine the crossing point of two modulus (G' and G'') at which gelling time and beginning of sample flow are determined (Mezger, 2011). The melting temperature of cheese is also an important quality parameter that characterizes the readiness for implementation and transition of the product from one processing step to another (Karoui et al., 2003).

The most common methods to determine the rheological properties of cheeses are dynamic and transient tests (Venugopal and Muthukumarappan, 2003). Textural and rheological characteristics of cheeses can also be studied using compression (Kulmyrzaev et al., 2005; Campanella et al., 1987; Buffa et al., 2001) and extensional (Ak et al., 1993; Muliawan and Hatzikiriakos, 2007) tests. Rheological properties of cheeses can be measured using small amplitude oscillatory shear experiments (Joshi et al., 2004) and tube viscometry techniques (Leach et al., 2003). Despite the usefulness of these techniques, a major drawback is that they are tedious, destructive, invasive, time-consuming and require highly skilled operators (Strasburg and Ludescher, 1995; Purna et al., 2005).

Fluorescence spectroscopy is a highly sensitive, rapid, non-

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destructive and easy to use an analytical technique that provides information on the presence of fluorescent molecules (Lakowicz, 2006). Natural compounds that exhibit fluorescence in cheeses are vitamin A and tryptophan residues, which provide specific information on the physical state of triglycerides, and protein conformational changes (Lakowicz, 2006), respectively. For instance, the melting temperature of fat in cheese has been determined from vitamin A fluorescence spectra recorded at different temperatures (Karoui et al., 2003). Fluorescence spectroscopy has been considered to monitor rheological parameters (Karoui and Dufour, 2006), light-induced changes (Andersen et al., 2005), quality and ripening of cheeses (Kulmyrzaev et al., 2005) and their molecular structure and molecular changes throughout the ripening (Kulmyrzaev et al., 2005; Karoui et al., 2007).

Studies conducted earlier assessed the potential of front face fluorescence spectroscopy to predict rheological parameters of cheeses exhibited in LVE region only, i.e. the storage modulus G', loss modulus G'', and the loss factor $tg\delta = G''/G'$ (Karoui et al., 2003). Stress at fracture (σ_F), strain at fracture (ε_F), work to fracture (W_F) and modulus of deformability (E) of soft cheeses obtained conducting uniaxial compression also well correlate with fluorescence spectra (Kulmyrzaev et al., 2005). However, as mentioned earlier, cheese as a functional ingredient can be subjected to mechanical processing (mixing, extrusion, transportation in tubes etc.) at shear stresses that can cause disruption of cheese structure and flow. LVE range of viscoelastic materials ($G' = const$) is limited by the value of strain (shear) γ_L (Mezger, 2011). γ_L is the strain value at which the curve G' begins to deviate from the LVE plateau value ($G' = const$). At strain amplitudes higher than γ_L the structure of the sample changes irreversibly. Thus, the limiting value γ_L and corresponding to it the limiting value τ_L (yield stress) characterize the point at which the structure of the sample is deformed irreversibly. Therefore γ_L or τ_L is considered as a critical rheological parameter that provides knowledge on the ability of viscoelastic materials to resist applied external force (stress), i.e. the mechanical strength of the internal structure of materials. Commonly yield stress τ_L is used in industrial practice to characterize structure strength of viscoelastic materials (Mezger, 2011). Another significant rheological characteristic of viscoelastic materials determined by the oscillatory rheology is the flow point γ_F or flow stress τ_F. The flow point occurs as the crossover point $G' = G''$ at which the internal structure of the material is braking to such an extent causing the material to flow. In industrial practice the flow stress τ_F is used in engineering processing of viscoelastic materials at which high rate shear deformation occurs (mixing, extrusion, pumping through channels). Therefore, τ_L (yield stress) and τ_F (flow stress) are significant rheological characteristics of cheeses from both scientific and practical point of view.

The objective of this study was to investigate the potential of fluorescence spectroscopy to predict the rheological characteristics of semi-hard cheeses such as τ_L (yield stress), τ_F (flow stress), modulus G', and loss modulus G'' measured at three oscillation (yield stress, flow stress and LVE) regions using amplitude sweep oscillatory tests. Melting points measured using temperature sweep tests and chemical compositions of the cheeses were also predicted using fluorescence spectra of the cheeses. Principal Component Analysis (PCA) and Partial Least Squares Regression (PLSR) were applied to fluorescence spectra to extract information on rheological, chemical, and melting point of semi-hard cheeses.

2. Materials and methods

2.1. Cheese samples

Three kinds of pre-packed semi-hard cheese Tilsit ($n = 3$) with 20% (low-fat (LF), 45% (medium-fat (MF)) and 55% (high-fat (HF)) fat in dry matter (FDM) were obtained from a local supermarket. Each cheese piece was cut into three sample portions and one was used for rheological measurements, while second and third portions were used in measuring chemical composition and fluorescence spectroscopy, respectively. The samples were identified, vacuum packed and stored at 4 °C before conducting experiments.

2.2. Chemical analysis

The moisture, fat and protein content of cheese samples were measured. Moisture in cheese was determined by the oven drying method at 130 °C (AOAC International 948.12, 2000). Fat content was determined using an extraction procedure with petroleum ether in a Soxhlet apparatus (Distillation System Vapodest 20, Germany) according to AOAC 920.125 (AOAC International, 2000). Kjeldahl method (AOAC International 991.20, 2000) was applied to measure protein content using an Extraction Unit EV6 All/16 (Gerhardt, Germany). All chemical analyses were carried out on three replicates of each cheese sample and average values were taken.

2.3. Rheological measurements

The cheese samples were sliced into thin disks (2 mm thick and 25 mm diameter) and stored at 4 °C until analysis in plastic bags to prevent dehydration. The rheological measurements were conducted using an MCR 302 rheometer (Anton Paar, Graz, Austria) with a parallel plate measuring system PP25 (Ø 25 mm), and the Peltier temperature control unit (P-PTD 200/56). The results of the rheological measurements were analyzed using Rheoplus/32 V3.61 (Anton Paar Germany GmbH, D-73760 Ostfildern) software.

Cheese exhibits both elastic (G') and viscous (G'') behavior depending on deformation conditions (shear rate) (Guinee, 2011). Therefore, oscillatory tests were conducted to obtain additional information on the elastic behavior of the cheese samples. Amplitude sweep (AS) tests were performed at fixed angular frequency $\omega = 10$ rad/s and strain values varied as 0.01%-100%. Temperature was maintained at 25, 30, 35, 40, 45, 50, 55, 60, 65 and 70 °C. Oscillation tests were conducted in yield stress, flow stress, and LVE ranges and G', G'' and τ (yield stress) were measured. The oscillatory tests were performed in triplicate at a given temperature and average values of the measured characteristics were obtained.

Melting temperatures of the cheese samples were determined using temperature sweep (TS) test. The angular frequency (ω) and strain (γ) were set constant as 10 rad/s and 1%, respectively. The temperature ramp was 20–100 °C, in a heating rate of 1 °C per 3 min. Tests were performed in triplicate for each sample and the average values were taken.

2.4. Fluorescence spectroscopy

Fluorescence spectra were recorded using a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon, USA) provided with a single-position (56°) thermostatically controlled cell holder dedicated to front-face fluorescence. The temperature of the cell holder was controlled by a digital temperature controller (VWR, Model 1136D, USA) set at 25, 30, 35, 40, 45, 50, 55, 60, 65 and 70 °C. The cheese samples were cut into rectangular bar shaped specimens with 1 cm × 1 cm cross-section and 4.2 cm length in order to fit into a 5-ml quartz cuvette. The cheese specimens were placed in the quartz cuvette, transferred into the cell holder of the spectrofluorometer and upon reaching the desirable temperature fluorescence spectra were collected. Emission spectra of tryptophan residues (305–480 nm, excitation: 290 nm) and vitamin A (340–620 nm,